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Letter to the Editor

Comments on "Glycerol conversion to acrylonitrile by consecutive dehydration over WO₃/TiO₂ and ammoxidation over Sb–(Fe,V)–O", published by Liebig, C., Paul, S., Katryniok, B., Guillon, C., Couturier, J.-L., Dubois, J.-L., et al. in Applied Catalysis B: Environmental, 132–133 (2013) 170–182. doi:10.1016/j.apcatb.2012.11.035

Dear Editor,

We came across a paper published recently in *Applied Catalysis B: Environmental* that we read with great interest due to its direct relevance to our research. It is about the direct conversion of glycerol into acrylonitrile [1]; such a paper is co-authored by a group with experience in this reaction for they claimed the ammoxidation of glycerol to acrylonitrile in a single step [2]. We have successfully explored such a reaction in the liquid and in the vapor phase under conventional thermal and under microwave activation [3–5].

Reading their paper, however, we came across to some puzzling comments. Despite their own claim [2], they report that they cannot run the direct ammoxidation of glycerol in the following terms: "We tried several times to reproduce the results published by Bañares et al., but the experiments resulted always in full conversion of glycerol with the formation of only traces of the desired product ACN (2% of selectivity in a typical experiment) with the main product being CO₂ (50% in yield)." in page 170 of their manuscript. This means 50% CO₂ selectivity. To find out about the remaining products, we had to look at supplementary information: "On the other hand, the selectivity to acrylonitrile was only 2%. Other products observed were acetic acid (9%), acetonitrile (6%), propionitrile (3%) and carbon dioxide (50%). The mass balance was 96%". That makes a total of 69%; it is very important to know what makes the remaining 31% selectivity.

We had an initial surprise when we saw that they could not reproduce our data. Reading their manuscript we find contradictions, errors and evidences showing that they did not reproduce our catalyst. The differences in some catalyst descriptors would approach an order of magnitude.

While they indicate they could not reproduce our data; it should be interesting that they elaborate on what makes the difference between their new data and their claimed process, which runs: ". . . relates to a method for producing acrylonitrile by the ammoxidation of glycerol in gaseous phase. The method can be implemented in a single step. . .." [2].

1. The paper

The abstract of the paper indicates that ". . . Sb–V–O or Sb–Fe–O catalysts were developed and used . . .". The limited number of samples would talk of an exploratory work rather than a development. There is some characterization of the Sb–Fe–O system, namely XRD, XPS, BET and TPR for several Sb/Fe stoichiometries, while they report only BET area for only one Sb/V stoichiometry. Interestingly, the one Sb–V–O sample has a low Sb/V atomic ratio (0.8 *vs.* 1.0 in ours, they do not reproduce our system) and an extremely low BET area (*ca.* 2 m²/g *vs.* 134 m²/g in our system; this is a dramatic difference). We know the relevance of BET area and their paper draws the same conclusion about BET area for the Sb–Fe–O series. Their paper brings an exhaustive analysis on the relevance of reaction conditions for the Sb–Fe–O system and on the role of Sb/Fe stoichiometry, but it delivers very limited information on the Sb–V–O system. Supplementary information provides an additional XRD pattern of fresh Sb–V–O and Sb–Fe–O, and a single XRD pattern of the used Sb–Fe–O but no information about used Sb–V–O. Supplementary information provides the TG analysis of one precursor Sb–Fe–O to optimize its calcination temperature, but such study is not reported by the Sb–V–O system. Our search to understand differences with our work is not trivial due to the minimal screening of catalyst (*i.e.*, one bulk Sb–V–O catalyst).

2. Blank activity runs

The supplementary information provides blank activity data; these are limited to conversion values for both reactors. Unfortunately, there is no indication of which products form. The blank reaction delivers 70% conversion to unknown products, and decrease to *ca.* 50% to unknown products after 1 h on stream. This is odd. There is no indication why there is deactivation in a blank test – where there is no catalyst – which is an unexpected result. On the other hand, evaporation of glycerol spontaneously delivers acrolein, so we understand that the first reaction would probably deliver acrolein, which fate in the second reactor remains unknown.

3. The Sb/V atomic ratio

We assume they attempted the Sb–V–O system on the premise that they tried to reproduce our data. Literature tells that a Sb/V ratio as low as 0.8 is not particularly suited for ammoxidation, more on the contrary [6], and it is not the ratio we used in our work. The low Sb/V atomic ratio makes the presence of crystalline V₂O₅ likely (small domains would not be apparent to XRD, but are highly evident to Raman spectroscopy). V₂O₅ phase is undesired for this reaction for it is selective to total oxidation and decomposition products (CO, CO₂, and acetonitrile) as well as catalyzing the unselective conversion of NH₃ to N₂ [7,8]. The lowest Sb/V ratio before

crystalline V_2O_5 forms is typically performing best in a given series [9]. It should have been convenient that they use a more appropriate Sb/V ratio, or at least mimic our ratio if they planned to reproduce our work.

4. The specific surface area

They report that BET area is critical for this reaction, as shown in the data of the Sb–Fe–O system. There is only one Sb–V–O sample, with $2\,m^2/g$. We have run low area bulk and high area supported Sb–V–O systems for propane ammoxidation (there is major parallelism in catalytic formulations for propane and glycerol ammoxidation). BET area draws dramatic activity differences [6 *vs.* 10]. As a matter of fact not only total activity increases with area, but TOF number remains comparable [11]. The importance of BET area is documented in their paper for Sb–Fe–O series. If they used a Sb–V–O sample of $2\,m^2/g$ they did not reproduce our catalyst.

5. Contradiction on activity data reporting

There is a major flaw comparing their and our activity data in the supplementary information: "The glycerol conversion was 100% in all cases, which is in agreement with the results reported in the literature.†"; however, our paper reports conversion values ranging from 10.4% up to 87.2%, but never a 100%. This statement is wrong and openly contradicts our data.

6. Contradiction on the Sb–V–O based sample

The page 171 of the manuscript runs: "The antimony vanadium mixed oxide was prepared following the method described by Nilsson et al. [40].". However, the supplementary information indicates: "The direct ammoxidation of glycerol was performed at $400\,^\circ C$ in a fixed bed down-flow reactor (1 in. inner diameter) using 1 g of alumina supported $VSbO4$ catalyst prepared according to the tartric acid method described by Banares et al.". This is contradictory. Was it a bulk Sb–V–O catalyst prepared as described by Nilsson or was it an alumina-supported Sb–V–O catalysts prepared as described by us? The few data help solving the confusion.

- The XRD profile in the supplementary information by no means corresponds to an alumina-supported monolayer of Sb–V–O but to bulk Sb–V–O. Had it been an alumina-supported sample, its dispersion would have been very poor since XRD tell the presence of large $SbVO_4$ aggregates, not like those present on a monolayer of $SbVO_4$ on alumina, even at several monolayers [6]. Consequently, they are not reproducing our system.
- Based on the one BET datum (*ca.* $2\,m^2/g$), they have bulk Sb–V–O and not alumina-supported monolayer of Sb–V–O (*ca.* $134\,m^2/g$ in our case). They used a sample with a BET area *ca.* 70 times smaller than ours.

The contradiction in the text on the two different syntheses reported for one sample is solved by XRD and BET data. They did not use alumina-supported monolayer of Sb–V–O on alumina. Thus, they are not reproducing our system.

In summary, the Sb–V–O sample was not prepared following our method, the Sb–V–O was not supported on alumina, and the Sb–V–O sample had *ca.* 70 times less surface area than ours. We do not find it surprising that they could not reproduce our results if they did not reproduce our samples. The catalyst is radically different:

- They use bulk Sb–V–O catalysts with *ca.* $2\,m^2/g$ *vs.* our alumina-supported monolayer of Sb–V–O with $130\,m^2/g$
- Their Sb/V atomic ratio of 0.8 *vs.* 1.0 (any value below 1 is detrimental).
- They indicate that they always obtain 100% like us. However, our conversion is never 100% but up to 87.2%
- The report two totally different synthesis for a single Sb–V–O sample.

We find the statement "We tried several times to reproduce the results published by Bañares et al., but the experiments resulted always in full conversion of glycerol with the formation of only traces of the desired product ACN (2% of selectivity in a typical experiment) with the main product being CO_2 (50% in yield)." in page 170 of their manuscript leads to confusion in literature, discrediting our work and appear to stand on hardly any data.

Despite contradictions in the text, the experimental data tell that their Sb–V–O catalyst is by no means similar to ours. XRD, BET, composition, . . . all data are absolutely different. Do not expect the same results when you do something totally different. We understand that they mean that they did not reproduce our conditions and consequently did not get our results. The way statements are written in this article appears unfortunate to us, and stand on no experimental evidence; we consider that such statements should retracted.

The use of very different conditions leads to very different results. We would suggest the use of higher area Sb–V–O catalysts, on alumina, with an appropriate Sb/V atomic ratio since these variables are critical for the ammoxidation of glycerol as well as the ammoxidation of propane. We would be more than happy to host members of your group and get them acquaint with the preparation of a monolayer of antimony and vanadium oxides on alumina and with our catalytic test procedures.

Sincerely,

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